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**MOLECULAR MECHANICS CALCULATIONS FOR NITRO AND AMINO
SUBSTITUTED CONJUGATED SYSTEMS CONTAINING
OXYGEN AND NITROGEN**

T. Vladimiroff

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13. ABSTRACT (Maximum 200 words) The Army is interested in developing new energetic materials which are highly resistant to initiation by heat and shock. Some of the most stable energetic materials known to man can be characterized as nitroaromatics. However, molecules like TNT and TATB do not have enough energy to make good propellants. One way to increase the energy of a molecule is to achieve a more favorable oxygen balance. Thus it would seem reasonable to consider aromatic systems which incorporate oxygen or nitrogen into the aromatic ring. Nitro and amino substituted pyridines, diazines, triazines, tetrazines, pyrroles and furans are investigated. First the heat of formation for these new materials is computed using additivity rules and an estimate of the propellant performance is made. Then the method of molecular mechanics is used to calculate the structure and properties of the various isomers of these molecules. It is found that nitro groups placed next to each other increases the steric energy while an amine group placed between nitro groups stabilizes the system. Diamiontrinitropyridine seems to be a particularly attractive candidate molecule for use in low vulnerability propellants.				
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CONTENTS

	Page
Introduction	1
Thermodynamic Calculations	1
Molecular Mechanics	2
Results and Discussions	3
Conclusions	4
Plans for Future Work	5
References	17
Distribution List	19

FIGURES

1	Relative energy of the isomers of trinitropyridine in kcal/mole	11
2	Relative energy of the isomers of trinitroaminipyridine in kcal/mole	11
3	Relative energy of the isomers of trinitrodiaminopyridine in kcal/mole	12
4	Relative energy of the isomers of trinitrodiazines in kcal/mole	12
5	Relative energy of the isomers of trinitroaminodiazines in kcal/mole	13
6	Relative energy of the isomers of trinitrotriazines in kcal/mole	13
7	Relative energy of the isomers of dinitroaminotriazine in kcal/mole	13
8	Relative energy of the isomers of dinitrotetrazine and nitroaminotetrazine in kcal/mole	14
9	Relative energy of the isomers of dinitropyrrole in kcal/mole	14
10	Relative energy of the isomers of dinitrofuran in kcal/mole	15
11	Relative energy of the isomers of dinitroaminofuran in kcal/mole	15

INTRODUCTION

In order to satisfy the Army's insensitive munition requirements it may be necessary to develop new energetic materials which are highly resistant to initiation by heat and shock. Since we do not have a very good understanding of why some energetic materials are much less sensitive than other energetic materials it is necessary to proceed in a somewhat exploratory manner. Traditionally, candidate energetic materials were synthesized and tested. If the new compound was less sensitive than the previously known materials then scale up procedures were initiated in order to produce enough material to fabricate actual munitions. If the new material did not have any interesting new properties it was abandoned and the synthesis of new compounds was initiated. Now, a new element has been added to the equation. Theoretical chemistry has advanced to the point that it can be used to make predictions about new molecules that have yet to be synthesized. These calculations can be used as a guide to the synthetic chemist so that his efforts can be concentrated on the most promising candidate materials.

In previous work we have performed molecular mechanics calculations on nitramines (ref 1), nitroalkanes (ref 2) and nitroaromatics (ref 3) in order to determine the force field which holds these molecules together. Since, Nitroaromatics are some of the most stable energetic materials known, we decided to concentrate on these type of materials in order to discover possible candidate molecules for propellant applications. Of the known nitro aromatic compounds, only trinitrobenzene gives propellant performance which is similar to M30 (ref 3). However, an effort to devise analogous polymeric type structures (nitro substituted polyacetylenes) proved futile due to excessive steric interactions in these type of materials. Part of the problem with aromatic materials is that they tend to have a poor oxygen balance. Trinitrotoluene, is a fairly stable material, but it does not have enough oxygen to make a good propellant. In order to improve the oxygen balance, molecules which incorporate oxygen or nitrogen in the aromatic system are considered in this work. Another factor which may contribute to the stability of aromatic energetic materials is hydrogen bonding. TATB (ref 4) has an extensive networks of hydrogen bonds. In previous work (ref 3) we were unable to properly take these hydrogen bonds into account so the required hydrogen bonding parameters will also be developed here.

THERMODYNAMIC CALCULATIONS

In order to evaluate the propellant performance of a postulated material it is necessary to devise a method by which their heats of formation can be estimated. Since molecular mechanics does not give satisfactory heats of formation (ref 5) for conjugated, nitrogen-containing heterocyclic molecules, it was decided to use additivity rules for this task. Shaw (ref 6) developed the necessary parameters but since his

values give solid benzene a heat of formation of zero (our estimate is 9.4 kcal/mole) new parameters were developed. The group parameters in kcals/mole are as follows: (C-H) = 1.56, (C-NO₂) = -4.76, (N<) = 12.11, (H-N< pyrrole) = 12.96, (O< furan) = -23.14 and (C-NH₂) = -7.54. In order to evaluate these parameters heats of formation were taken from Shaw's paper and the value measured for s-triazine by Bystrom (ref 7) was used. The calculated heats of formation were used in conjunction with the recently developed thermochemical computer code (ref 8) to calculate the flame temperature and impetus. The calculated values are summarized in table 1. Molecules with a wide range of flame temperatures are available. Materials with a high flame temperatures can be used with a nonenergetic binder. For molecules with a flame temperature in the neighborhood of 3000K an energetic binder with a similar flame temperature would have to be found. Materials with an impetus considerably below 1000 Joules/gm. are excluded from further consideration due to their low energy. The best candidate for a low vulnerability propellant would be trinitrodiaminopyridine, if it can be synthesized and its stability proves to be similar to TATB.

MOLECULAR MECHANICS

The chemical compounds listed in table 1 were further investigated using the method of molecular mechanics. Allinger's MM2(87) force field was used which was specifically designed to handle aromatic nitrogen (ref 5), aromatic oxygen (ref 9) and hydrogen bonding (ref 10). Molecular parameters developed in previous work (ref 3) were employed. Hydrogen-bonding distance parameter for the interaction of a nitro group oxygen atom and an amine hydrogen was set to 2.0Å. The analogous parameter for the hydroxyl-nitro group interaction was set at 1.95Å. The depth of the attractive well was adjusted to 2.42 kcal/mole for both hydrogen bonds. As already noted for nitramines (ref 1), molecular mechanics does not have a satisfactory method by which amine groups can be represented. The amine group is puckered in aniline so that it is best represented by sp³ hybridization of the nitrogen atom and a lone pair of electrons (ref 3). The amine groups are found to be planar in TATB (ref 4) and 2,4,6-trinitroaniline (ref 11). Since we are primarily interested in the interaction between amine groups and nitro groups, amine groups were taken to be planar in this work. The H-N-H angle parameter was set to 124 degrees and the C-N-H angle parameter was set to 118 degrees. A lone pair of electrons was not included on the amine nitrogen.

These new parameters and the parameters developed for aniline (ref 3) and nitrobenzene (ref 3) were used to calculate the structures of 2,6-dinitrophenol, 2,4,6-trinitroaniline and 3,5-dinitropyridine. The calculated bond lengths and bond angles are compared to experimental values determined by X-ray diffraction techniques. The agreement with experiment is fairly good except for the case of the amine group in trinitroaniline. For this group the calculated C-N bond distance is too

long by 0.054Å, the C-C(NH₂)-C angle is too large by 3.6 degrees and the H-N-H angle is too small by 4.2 degrees. The hydrogen bond distance is also predicted to be too long, although it should be pointed out that this distance was not measured with a great deal of accuracy. It is not known if the amine groups in aniline and trinitroaniline are inherently different or if the distortions are caused by the crystalline field. Therefore, it was decided that the discrepancies were not sufficiently serious to require further adjustment of the parameters which describe the amine group.

RESULTS AND DISCUSSIONS

Recently trinitropyridine has been synthesized (ref 12). We decided to calculate the relative energies of all the isomers of this molecule. Our calculations are presented in figure 1. It was found that the isomers with three adjacent nitro groups have the highest energy. The isomers with two adjacent nitro groups have a lower energy and the 2,4,6-trinitropyridine has the lowest energy. Our calculations show that Licht and Ritter (ref 12) synthesized the lowest energy isomer. The effects of adding an amine group were investigated next. The results are depicted in figure 2. Again the highest energy isomers have three nitro groups adjacent to each other. The amine group has a stabilization effect when placed between two nitro groups and the isomer with the lowest energy is obtained when no nitro groups are next to each other and there is an amine group between two of the nitro groups. The effects of an additional amine group were also investigated. It was found that the lowest energy isomer is the 3,5-diamino-2,4,6-trinitropyridine as illustrated in figure 3. If this molecule will form a hydrogen bonded network similar to TATB it may prove to be a very attractive candidate for insensitive propellant applications.

Trinitro substituted diazines were also considered. 1,2-Diazine and 1,4-diazine substituted with three nitro groups are the least stable because these geometries dictate that two nitro groups must be placed next to each other. The 1,3-diazine has one isomer which has no nitro groups next to each other and is calculated to have the lowest energy. The relative energies of all the isomers of this molecule are displayed in figure 4. The effects of amine substitution were considered next. The results are presented in figure 5. The amine group has no effect when it is placed in a position which is not adjacent to a nitro group and is most effective when placed in a position between two nitro groups. The 2,4,6-trinitro-5-amino-1,3-diazine is found to be the most stable.

The three possible isomers of trinitrotriazine have been depicted in figure 6. The energy decreases in a regular manner as the progression is made from the 1,2,3-triazine to the 1,3,6-triazine because the interaction between nitro groups diminishes. The replacement of one of the nitro groups with an amine group is considered next. The highest energy is obtained when two nitro groups are next to

each other. The lowest energy is obtained for the dinitroamino-1,3,6-triazine as can be seen in figure 7. No evidence for the synthesis of the 1,2,3,4 or the 1,2,3,5-tetrazine was found in the literature, however this is not a serious deterrent for a theoretical study. All possible isomers of dinitrotetrazine and nitroaminotetrazine were considered. The computed steric energies are reported in figure 8. The dinitro 1,2,3,4-tetrazine was found to have the highest energy, but substituting an amine group for one of the nitro groups produced the isomer with the lowest energy. It is not clear why the symmetric dinitrotetrazine has a higher energy than the 1,2,3,5-dinitrotetrazine.

Finally, various isomers of pyrrole and furan were considered. The introduction of oxygen into the aromatic ring in furan promotes a more favorable oxygen balance thus making this molecule more energetic than the analogous pyrrole. As can be seen from table I, dinitroaminofuran has a flame temperature above 3000K but dinitroaminopyrrole does not. We have presented the results of our molecular mechanics calculations for dinitropyrrole in figure 9. The highest energy isomer is the 3,4-dinitropyrrole and the lowest energy isomer is the 2,5-dinitropyrrole. An analogous trend is observed for dinitrofuran as can be seen in figure 10. The various isomers of dinitroaminofuran are depicted in figure 11. It is found that the isomers with adjacent nitro groups have the highest energy and that the 2,5-dinitro3-aminofuran has the lowest energy.

CONCLUSIONS

Energetic aromatic molecules such as TNT and TATB are quite stable but their oxygen balance is such that there is not enough energy in these materials to make a modern propellant. In this work an attempt was made to find new energetic materials which retain the insensitivity inherent in aromatic systems but have an oxygen balance more suitable for propellant application. The strategy employed was to incorporate oxygen or nitrogen into the aromatic system. Various nitro and amino substituted pyridines, diazines, triazines, tetrazine, pyrroles and furans were considered. Simple group additivity rules were devised based on the work of Shaw in order to approximate the heat of formation for these molecules. Then our thermodynamic code was used to estimate the flame temperature and impetus. It was found that a wide range of flame temperatures was possible with these materials. The additivity rules do not take into account the interactions between groups. A molecular mechanics method was used to calculate these interactions in order to find the isomers with the lowest relative energy. It was generally determined that nitro groups placed next to each other have a high energy of interaction while amine groups placed between nitro groups tend to stabilize the system. Based on our calculations and the analogy with TATB, 2,4,6-trinitro-3,5-diaminopyridine looks like a promising material for propellant applications if it can be synthesized and a suitable binder can be found.

PLANS FOR FUTURE WORK

Ab initio studies have appeared in the literature in order to study the protonation of azines (ref 15) and the binding energy of Li^+ to azines (ref 16). The addition of nitro and amino substituents to azines makes ab initio calculations too expensive to be performed for these types of molecules. That is why the molecular mechanics method was chosen for these calculations which requires an order of magnitude less computer time and is comparable in accuracy to ab initio methods using small basis sets. However, it should be pointed out that the molecular mechanics method was originally applied to hydrocarbons. In aromatic systems with electronegative substituents, a significant amount of charge transfer may take place which is not always properly taken into account by our force field. Therefore, it might be interesting to perform some limited ab initio studies on the molecules considered in this work in order to confirm some of our results. Another recent development has been the introduction of the MM3 force field by Allinger and coworkers (ref 17, 18, and 19). This new and improved force field promises to make more accurate calculations possible on vibrational frequencies (ref 18) and crystals (ref 19). MM3 should be extended to include energetic materials where calculations on crystal are very important. In order to correctly predict the rotation of the nitro groups out of the plane of the aromatic ring the whole crystal has to be taken into account. The calculation of the density of a new energetic material is important in order to predict explosive performance. Finally, the heat of sublimation which is calculated as the energy which holds the crystal together is required to convert a gas phase heat of formation to a solid state heat of formation. Our intention is to explore these refinements in greater detail.

Table 1. Calculated flame temperatures and impetuses for some nitro and amino substituted conjugated heterocyclic molecules.

<u>Molecule</u>	<u>Flame temperature (K)</u>	<u>Impetus Joules/gm</u>
dinitropyridine	2651	901
trinitropyridine	3840	1195
trinitrodiamino pyridin	3041	1034
dinitrodiazine	3175	1074
trinitrodiazine	4340	1207
trinitroamino diazine	4021	1176
dinitrodiamino diazine	2385	874
trinitrotriazine	4268	1095
dinitroamino triazine	3632	1137
dinitrotetrazine	4215	1111
nitroamino tetrazine	2801	974
dinitropyrrole	3123	1069
dinitroaminopyrrole	2553	966
dinitrodiamino pyrrole	2309	856
dinitrofuran	3604	1138
dinitroaminofuran	3077	1034

Table 1. (cont)

<u>Molecule</u>	<u>Flame temperature (K)</u>	<u>Impetus Joules/gm</u>
dinitrodiamino furan	2659	939
trinitroanalyn	2697	968
diaminotrinitro benzene	2398	882
triaminotrinitro benzene	2205	825
dinitroaniline	2019	693
picric acid	3162	1032
M30	3005	1076

Table 2. Experimental and calculated data on substituted aromatic molecules.

	2,6-dinitrophenol		2,4,6-trinitro aniline		3,5-dinitropyridine	
	<u>MMP2</u>	<u>ref(13)</u>	<u>MMP2</u>	<u>ref(4)</u>	<u>MMP2</u>	<u>ref(14)</u>
bond ^a						
C-C	1.402	1.389	1.399	1.392	1.398	1.370
C-NO ₂	1.490	1.467	1.487	1.468	1.480	1.468
C-NH ₂			1.394	1.340		
C-OH	1.360	1.340				
C-N					1.342	1.328
C-H	1.103	.94	1.102	.98	1.102	0.96
hydrogen bond	1.89	1.84	1.94	1.83		
angle ^b						
C-N-C					117.4	117.4
C-C(NO ₂)-C	123.4	122.1	122.6	123.8	121.3	121.2
C-C(NH ₂)-C			116.6	113.0		
C-C(OH)-C	115.0	116.0				
C-C-C	119.4	119.9	117.8	118.2	114.8	115.8
O-N-O	123.9	122.9	123.8	123.5	124.4	124.8
H-N-H			122.7	126.9		
NO ₂ twist	0.0	13.1, 2.67	0.0	8.5, 4.0 22.5	0.0	7.0, 1.5

^aBond length are in Angstroms.

^bBond angles are in degrees.

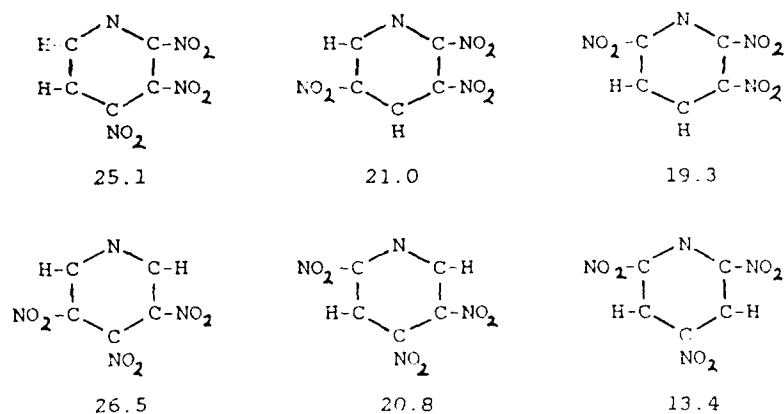


Figure 1. Relative energy of the isomers of trinitropyridine in kcal/mole

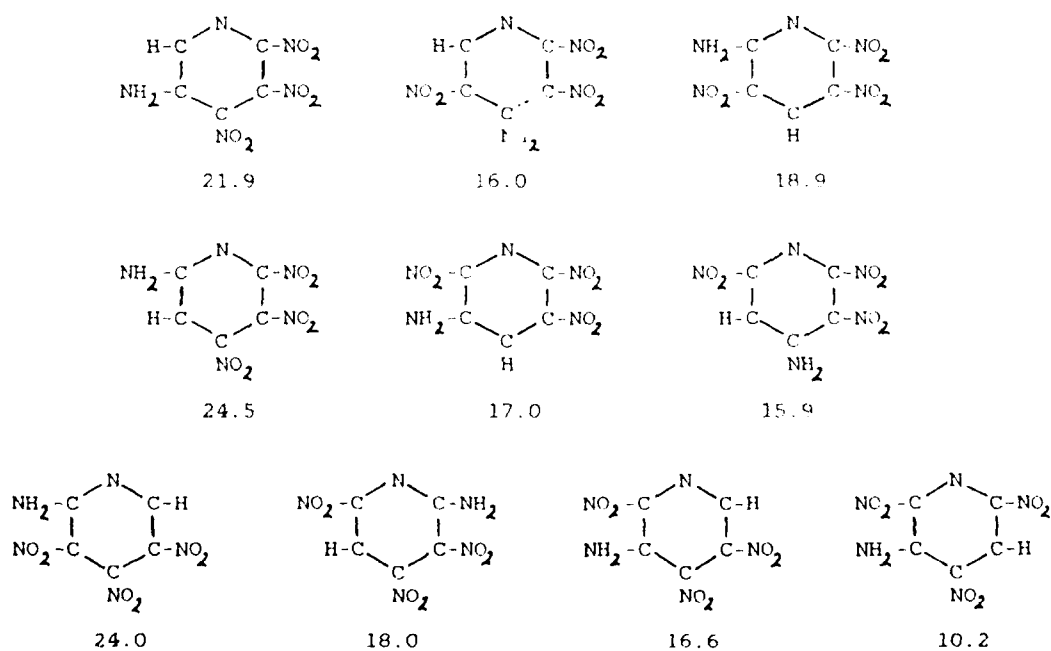


Figure 2. Relative energy of the isomers of trinitroaminipyridine in kcal/mole

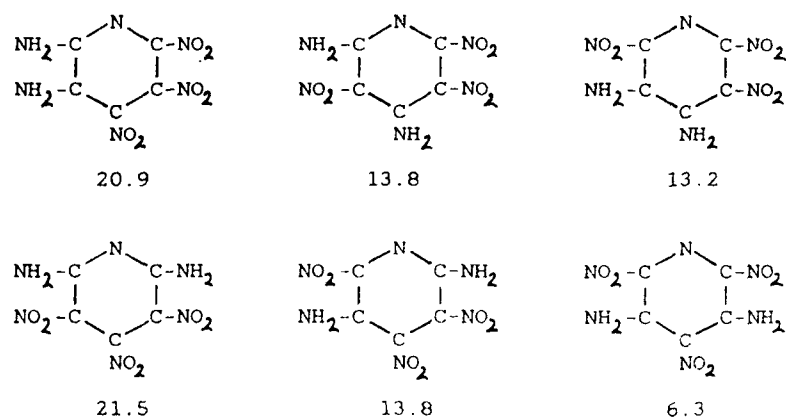


Figure 3. Relative energy of the isomers of trinitrodiaminopyridine in kcal/mole

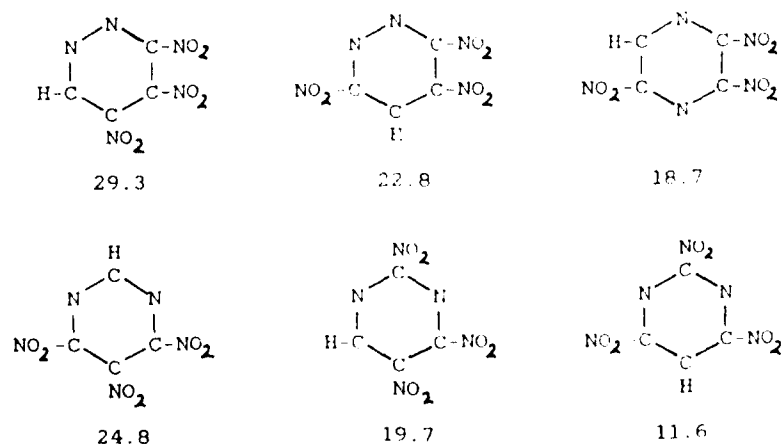


Figure 4. Relative energy of the isomers of trinitrodiazines in kcal/mole

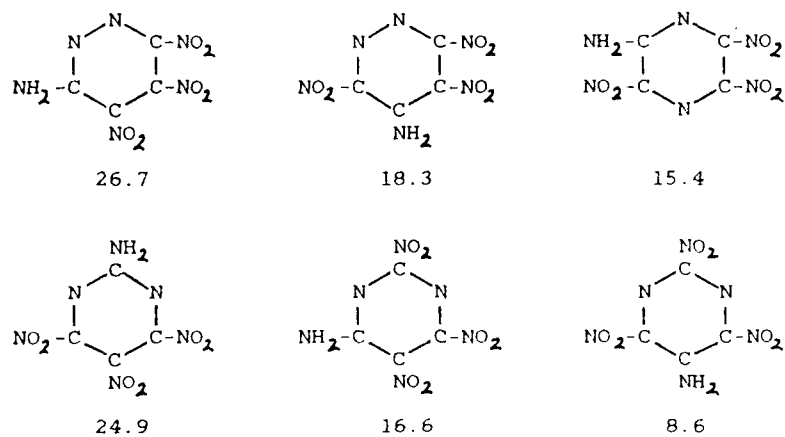


Figure 5. Relative energy of the isomers of trinitroaminodiazines in kcal/mole

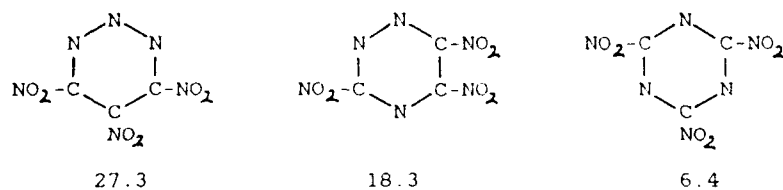


Figure 6. Relative energy of the isomers of trinitrotriazine in kcal/mole

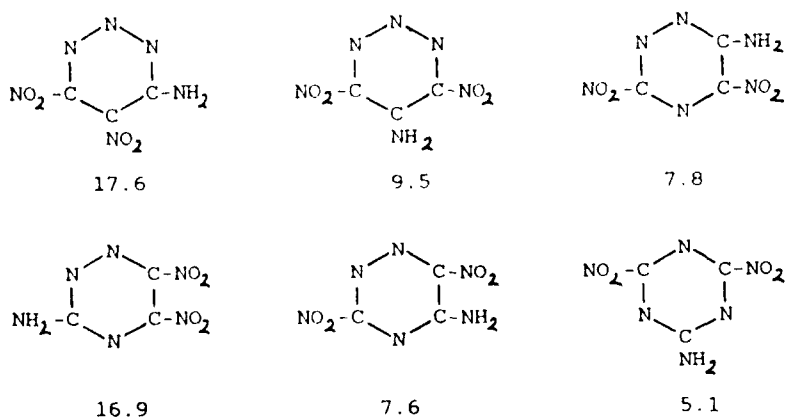


Figure 7. Relative energy of the isomers of dinitroaminotriazine in kcal/mole

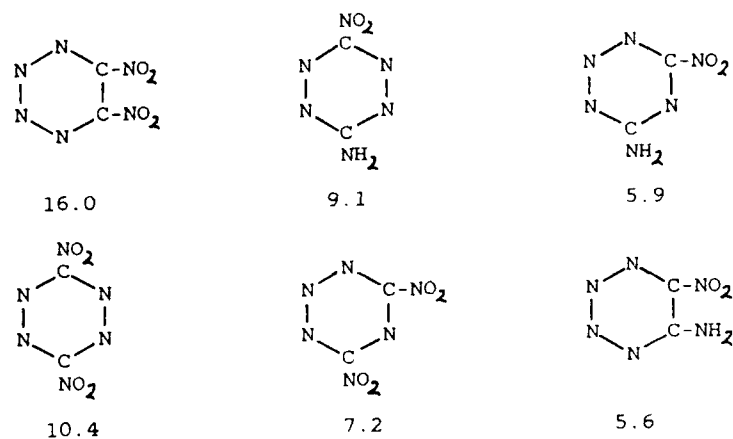


Figure 8. Relative energy of the isomers of dinitrotetrazine and nitroaminotetrazine in kcal/mole

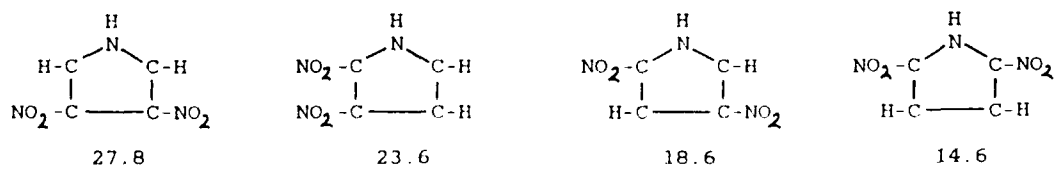


Figure 9. Relative energy of the isomers of dinitropyrrole in kcal/mole

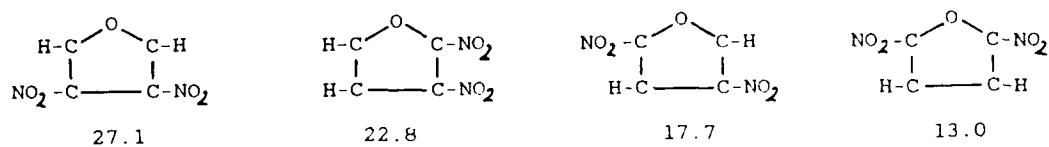


Figure 10. Relative energy of the isomers of dinitrofuran in kcal/mole

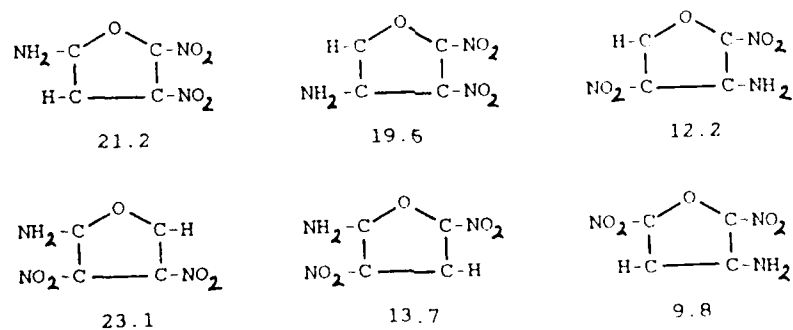


Figure 11. Relative energy of the isomers of dinitroaminofuran in kcal/mole

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